

GLOBAL SOURCES AND SINKS OF OCS AND CS<sub>2</sub>  
AND THEIR DISTRIBUTIONS

Mian Chin<sup>1</sup> and D. D. Davis

School of Earth and Atmospheric Sciences, Georgia Institute  
of Technology, Atlanta

**Abstract.** This study investigates the distribution and magnitudes of the global sources and sinks of OCS and CS<sub>2</sub>. From an analysis of the correlations between measured emission rates and environmental parameters, the sources of OCS and CS<sub>2</sub> are estimated to be 1.23 (0.83-1.71) Tg(OCS) yr<sup>-1</sup> and 0.57 (0.34-0.82) Tg(CS<sub>2</sub>) yr<sup>-1</sup>, respectively. Our results indicate that 30% of the atmospheric OCS source is derived from the oxidation of CS<sub>2</sub>, while emissions from the ocean and other natural terrestrial sources contribute 28% and 24%, respectively. In the case of CS<sub>2</sub>, the major source is from chemical industrial emissions (58%) while the ocean contributes about 34% to the total CS<sub>2</sub> source. Our estimate of the OCS and CS<sub>2</sub> emission rates suggests that anthropogenic activities contribute approximately 32% to the total OCS source. The major sink for CS<sub>2</sub> is oxidation by tropospheric OH, whereas, that for OCS appears to be uptake by vegetation.

1. INTRODUCTION

Carbonyl sulfide (OCS) is the most abundant sulfur gas in the atmosphere. While relatively inert in the troposphere, OCS transported into the stratosphere followed by photo-

dissociation and photooxidation is believed to be the major source of stratospheric background sulfur aerosol [Crutzen, 1976; Turco et al., 1980; Hofmann, 1990]. Stratospheric aerosol influences the Earth's radiation balance, and hence its climate, and may also provide surfaces for heterogeneous reactions that could affect stratospheric ozone levels [Turco et al., 1982; Rodriguez et al., 1991]. Because OCS may play a significant role in forming stratospheric aerosol, the understanding and quantification of its sources, sinks, lifetimes, and global budget are of considerable scientific importance.

Many natural and anthropogenic sources of OCS, such as oceans, soils, volcanoes, biomass burning, and industrial processes, have been identified. In addition to these direct sources, the oxidation of CS<sub>2</sub> in the atmosphere is also believed to be a significant source of OCS. For example, laboratory studies have shown that the conversion efficiency of CS<sub>2</sub> to OCS is 0.81 [Chin, 1992]. Thus the fact that CS<sub>2</sub> is a source of OCS makes it necessary to estimate the global source strength of CS<sub>2</sub>, both natural and anthropogenic, before the total source strength of OCS can be evaluated.

In the past decade, considerable work has been done to quantify these sources see, for example, Adams et al. [1981], Ferek and Andreae [1983], Steudler and Peterson [1985], Johnson and Harrison [1986], Kim and Andreae [1987], Goldan et al. [1987], Lamb et al. [1987], and Staubes et al. [1989]. Even so, large uncertainties still remain. For example, fluxes from the ocean are usually calculated by air-sea exchange models [e.g., Liss and Slater, 1974] using the measured seawater and atmospheric concentrations of the sulfur compound as well as the

<sup>1</sup>Presently at Division of Applied Sciences, Harvard University, Cambridge, Massachusetts.

transfer velocity for that compound. However, there are significant variations in the measurement data, and uncertainties remain in the evaluation of the transfer velocity. The terrestrial emissions of OCS and CS<sub>2</sub> are a function of many environmental conditions such as temperature, moisture, soil, and vegetation type; thus there are significant difficulties in quantifying these sources due to problems in measurement techniques and a lack of knowledge of the microbiological processes for releasing and uptaking these sulfur gases. Anthropogenic sources of OCS and CS<sub>2</sub> also have drawn considerable attention and speculation in the past decade [Turco et al., 1980; Khalil and Rasmussen, 1984; Hofmann, 1990; Bingemer et al., 1990]; however, because very little has been done to both identify and quantify these sources, estimating their global magnitude has again involved extrapolations based on very limited data [Turco et al., 1980; Khalil and Rasmussen, 1984].

The major tropospheric sink of CS<sub>2</sub> is its reaction with OH radicals. For OCS the most important loss processes involve stratospheric photolysis and reaction with O atoms and OH radicals, together with tropospheric uptake by vegetation [Brown and Bell, 1986; Goldan et al., 1988]. However, the latter loss mechanism still involves considerable uncertainty. For example, at present only limited laboratory studies are available on OCS deposition to agriculture crops and grass [Goldan et al., 1988; Kesselmeier, 1992] and very few field measurements exist that quantify the vegetation uptake of OCS [Mihalopoulos et al., 1989; Hofmann et al., 1992; Castro and Galloway, 1991; Berresheim and Vulcan, 1992].

In this work a detailed reexamination of the sources and sinks of OCS and CS<sub>2</sub> as a function of latitude has been carried out. A follow-on exercise has involved using this information as input to a two-dimensional, nine-box atmospheric model [Chin, 1992]. The latter model was used to examine the consistencies or the lack thereof in observed atmospheric concentration levels, surface emissions, atmospheric circulation and destruction of OCS.

In the work reported here, we adopted the following approach:

1. The planetary atmosphere was divided into four major latitudinal regions: 90°-30°N, 30°N-0°, 0°-30°S, 30°-90°S. For purposes of evaluating the effects of temperature and ecosystem types, each of these major regions was then further divided into 15° or 30° latitudinal subdivisions. For example, to resolve the temperature dependence of sulfur gas releases in the region 90°-30°N, we summed the estimated emissions from 90°-75°N, 75°-60°N, 60°-45°N, and 45°-30°N subdivisions.

2. For each subdivision, we evaluated the following physical or biological parameters: (1) the maximum,

- minimum, and mean temperature [Pearce and Smith, 1984]; (2) soil types [Donahue et al., 1977], marshland characteristics (The Times, *Atlas of the World*, 1980), agriculture crops [U.S. Department of Agriculture, 1987], vegetation types [Whittaker and Likens, 1975; 1984], and ocean productivity [Koblentz-Mishke et al., 1970]; and (3) relevant to human activities and industrial capacities [1990 *Britannica Book of the Year*, Encyclopedia Britannica Inc., Chicago, 1990; *United Nations Statistical Yearbook*, 1973-1986].

3. Emission or uptake fluxes for OCS and CS<sub>2</sub> were evaluated for each subdivision according to correlations between field measured fluxes and the parameters obtained from (2). A detailed analysis of our OCS and CS<sub>2</sub> sources and sinks findings is presented in the text that follows.

## 2. SOURCES OF OCS AND CS<sub>2</sub>

### 2.1. Oceans

The ocean is believed to be a source of both OCS and CS<sub>2</sub> since their observed concentrations in ocean water are almost always supersaturated [Andreae, 1985, 1987]. Here we summarize the estimated ocean fluxes of OCS and CS<sub>2</sub> in the literature, analyze the uncertainties associated with them, and provide revised estimates of their magnitudes.

**2.1.1. Carbonyl sulfide.** The concentration of OCS in surface ocean water has been reported to be in the range of 10 to 1000 pmol L<sup>-1</sup> [Rasmussen et al., 1982; Ferek and Andreae, 1983; Turner and Liss, 1985; Johnson and Harrison, 1986]. It has been suggested that the ocean could be a sink for atmospheric OCS because of its hydrolysis at the slightly alkaline pH of seawater [Rowland, 1979; Johnson, 1981]. An argument against this hypothesis is the observation that the ocean is supersaturated in OCS in coastal and open ocean water, except in regions of low biological productivity, at night, and during high-wind conditions [Andreae, 1985]. In earlier work, it was suggested that OCS was produced in the ocean by the photochemical oxidation of dissolved organic sulfur compounds, and as a result that there could be a diurnal variation in its surface water concentrations by up to 1 order of magnitude [Ferek and Andreae, 1984]. Still more recently a study by Zepp and Andreae [1989] indicates that OCS is formed by the photosensitized oxidation of organosulfur compounds, including mercaptans, that do not directly absorb sunlight.

As is true for other marine sources of atmospheric trace gases, the flux of OCS from ocean water to the atmosphere has never been measured directly; instead, it is calculated from air-sea exchange models that parameterize the transfer as a first-order loss as shown in equation (1) [Liss and

TABLE 1. Summary of OCS and CS<sub>2</sub> Flux from the Ocean (Tg(OCS) yr<sup>-1</sup> or Tg(CS<sub>2</sub>) yr<sup>-1</sup>) in the Literature

Location	Season	R <sub>ss</sub> <sup>a</sup>	k, <sup>†</sup> cm hr <sup>-1</sup>	Total Flux From Ocean, Tg yr <sup>-1</sup>	Reference <sup>‡</sup>
<i>OCS Flux</i>					
		1.4(open ocean)		0.6±0.3	1
		3.4(coastal)			
Pacific	spring	1.5-3	11.9	0.2-0.4	2
Peru coast	summer	2.6(upwelling)	20	0.87	3
World oceans		1.5(open ocean)	15	0.64	4
		1.9(transition)			
		2.6(upwelling)			
		10.5(coastal/shelf)			
North Sea coastal	spring-summer	4.6			5
<i>CS<sub>2</sub> Flux</i>					
North-Atlantic	spring-fall		11.7	0.13-0.52	6

<sup>a</sup>R<sub>ss</sub> is the super saturation ratio, see text for definition.<sup>†</sup>K is the transfer velocity, see text for definition.<sup>‡</sup>References are 1, Rasmussen et al., [1982]; 2, Johnson and Harrison [1986]; 3, Ferek and Andreae [1983]; 4, Andreae [1986]; 5, Turner and Liss [1983]; 6, Kim and Andreae [1987].

Slater, 1974; Bates et al., 1987; Saltzman and Cooper, 1989]:

$$F = k \left( \frac{c_g}{H} - c_l \right) \quad (1)$$

Here k is the transfer coefficient (or piston velocity); H is dimensionless Henry's law constant defined as the equilibrium concentration in the gas phase divided by the equilibrium concentration in the liquid phase; and  $c_g$  and  $c_l$  are the measured concentrations in the gas and liquid phases, respectively. Equation (1) can also be expressed as

$$F = k \frac{c_g}{H} (1 - R_{ss}) \quad (2)$$

where  $R_{ss}$  is the supersaturation ratio, defined as  $H \cdot c_l / c_g$ . The transfer coefficient k is proportional to the diffusivity D of the gas in seawater. In most studies, the transfer velocity of OCS is determined by scaling it to the transfer velocity of dimethyl sulfide (DMS), which is also scaled to the average transfer velocity of radon [Andreae and Raemdonck, 1983; Andreae, 1986]. In this case, the estimated uncertainty in the flux calculations related to the transfer coefficient k could be as large as a factor of 2 [Kim and Andreae, 1987].

On the basis of equation (2) and available marine OCS measurements, the flux of OCS from the ocean was estimated to be in the range of 0.2 - 0.9 Tg(OCS) yr<sup>-1</sup> [Rasmussen et al., 1982; Ferek and Andreae, 1984; Johnson

and Harrison, 1986; Andreae, 1985, 1986]. Rasmussen et al. [1982] measured an average super saturation ratio of 3.4 for coastal water and 1.4 for open ocean water; they also estimated the worldwide flux of OCS at  $0.6 \pm 0.3$  Tg(OCS) yr<sup>-1</sup>, assuming that the fraction of the coastal water area was 0.15. During a summer ship cruise along the Peru coastal area, Ferek and Andreae [1984] found the average supersaturation ratio of OCS to be 2.6 (ranging from 1.5 to 5.7). They estimated the global OCS emission from the ocean to be 0.87 Tg OCS yr<sup>-1</sup>, assuming an average supersaturation of 2 for the entire ocean and a transfer coefficient of 20 cm hr<sup>-1</sup>. A lower value of 0.2-0.4 Tg(OCS) yr<sup>-1</sup> was obtained by Johnson and Harrison [1986], who estimated that the global mean supersaturation ratio of OCS in the surface ocean water was 1.5-3, based on measurements in the Pacific which included both coastal and open ocean areas. The transfer velocity they used was 12 cm hr<sup>-1</sup>. A still later estimate of the OCS source strength from the ocean was given by Andreae [1985, 1986], this estimate being based on a more comprehensive set of marine OCS measurements. On the basis of these new measurements and using a transfer velocity of 15 cm hr<sup>-1</sup>, Andreae estimated the OCS fluxes from oligotrophic, transition, upwelling, and coastal/shelf areas. For this case the estimated total flux from the ocean was 10.7 Gmol yr<sup>-1</sup> (0.64 Tg(OCS) yr<sup>-1</sup>). All reported OCS ocean flux estimates are summarized in Table 1.

On the basis of all available marine OCS data, it would now appear that the OCS flux from the ocean as estimated by Andreae [1985] may still be too high. The reasons for

this are as follows: First, seasonal variations were not adequately taken into consideration. Because OCS production is light intensity dependent, its production in seawater is expected to be higher in the summer and lower in the winter. Andreae's estimate was based on measurements in summer (1983) and spring (1984) months only, no winter time measurements were available. In fact, limited winter time measurements suggest that parts of the ocean may be a sink for OCS during winter months (R. J. Ferek, personal communication, 1991; M. O. Andreae, personal communication, 1992). Second, because the supersaturation ratio (10.5) in the coastal and shelf water observed by Andreae [1986] was much higher than for other reported coastal water values (for example, 3.5 by Rasmussen et al. [1982], and 4.6 by Turner and Liss [1985]), it may not be representative of the global average value for coastal water. On the basis of these considerations, in this study we have reduced the OCS flux from the ocean by a factor of 2, e.g. 0.32 Tg(OCS) yr<sup>-1</sup> with a range of 0.16 to 0.64 Tg(OCS) yr<sup>-1</sup>.

**2.1.2. Carbon disulfide.** There are currently only very limited measurements of CS<sub>2</sub> in seawater. Lovelock [1974] reported an average concentration of 7 pmol L<sup>-1</sup> for 35 samples from the open Atlantic ocean. Bandy et al. [1982] measured a much higher value in coastal water (120 pmol L<sup>-1</sup>, n=1) and marsh water (950 pmol L<sup>-1</sup>, n=3). Kim and Andreae [1987] reported mean concentrations of CS<sub>2</sub> in the open ocean and coastal and shelf waters of the North Atlantic ocean from April to September as 8±4 (n=95) and 16.5±9.5 (n=110) pmol L<sup>-1</sup>, respectively. More recently, Kim and Andreae [1992] have reported on the analysis of several subsets of the latter data base, the results of which have shown a very strong trend of decreasing concentration levels of CS<sub>2</sub> in going from estuaries to coastal areas to the open ocean, i.e., a factor of 4 for the month of September. Using the air-sea exchange model (equation (2)) with a coastal and shelf area fraction of 0.15 and an estimated transfer velocity of 11.7 cm hr<sup>-1</sup>, Kim and Andreae [1987] have estimated the CS<sub>2</sub> flux from the ocean to be 3.4 (1.7-7) Gmol CS<sub>2</sub> yr<sup>-1</sup>, equivalent to 0.25 (0.13-5.0) Tg(CS<sub>2</sub>) yr<sup>-1</sup>. Again, possible seasonal and diurnal variations were not considered in this study. The seasonal variations in seawater concentrations of CS<sub>2</sub> observed by Kim and Andreae between spring and fall appear to be in general agreement with the seasonal variation of ocean productivity (e.g., as monitored by NOAA-7's visible and near infrared biological satellite imager, C. J. Tucker, NASA/GSFC), and this suggests that there are significant seasonal variations in the CS<sub>2</sub> ocean flux. Thornton and Bandy [1991] observed diurnal variations in CS<sub>2</sub> concentration levels in the atmosphere over the ocean (e.g., lower at night or in the early morning, and higher during the day), an

observation that led these authors to speculate a photosynthetic source of CS<sub>2</sub> in the sea surface. In this study, as a result of considering the likely seasonal and diurnal variations in CS<sub>2</sub>, a 30% lower value was estimated for the CS<sub>2</sub> flux than given by Kim and Andreae [1987] (i.e., 0.18 with a range of 0.09-0.36 Tg(CS<sub>2</sub>) yr<sup>-1</sup>).

## 2.2. Soils and Marshes

Almost all emissions from land areas, i.e., soil and vegetation, have been measured using an enclosure technique (see, for example, Adams et al. [1981], Goldan et al. [1987], and Lamb et al. [1987]). This technique involves an open-bottomed chamber covering an area of soil, marsh or vegetation, in which carrier gas is passed through the enclosure that is usually, but not necessarily, free of the species of interest, e.g., OCS and CS<sub>2</sub> in this case. The flux from the surface covered by the enclosure is determined using the equation:

$$F = \frac{Q}{A} (C_{out} - C_{in}) \quad (3)$$

where F is the flux; Q is the carrier gas flow rate; C<sub>in</sub> is the sulfur concentration in the carrier gas flowing into the enclosure; C<sub>out</sub> is the sulfur concentration in the gas mixture flowing out of the enclosure; and A is the area covered by the enclosure. As noted by other workers, while this enclosure technique is the most practical method for measuring the surface flux, it has the disadvantage of disturbing the natural microclimate. For example, when sulfur-free air is used as the carrier gas in an enclosure [Adams et al., 1981; Goldan et al., 1987; Lamb et al., 1987; Staubes et al., 1989], it creates an artificial sulfur concentration gradient, and the diffusion of sulfur gases into the enclosure may then be enhanced resulting in an overestimate of the flux. The larger the difference between the concentration in ambient air and the concentration within the measurement chamber, the greater this potential problem can become. This suggests that the problem in measuring OCS fluxes should be more severe than for measuring CS<sub>2</sub> fluxes when using this type of measurement. In addition to the above problem, the latter technique also does not measure the uptake of sulfur gas by the surface. Because of the aforementioned problems involving sulfur-free air, ambient air has been employed by some investigators [Stedler and Peterson, 1984, 1985; Castro, 1990; Castro and Galloway, 1991]. In the latter case, however, the concentration levels C<sub>in</sub> and C<sub>out</sub> of the sulfur gas being measured are often nearly the same; therefore, the evaluation of the flux from equation (3) involves obtaining the difference between two large numbers. As noted by

TABLE 2. Summary of Measured OCS and CS<sub>2</sub> Fluxes From Soils and Marshes in the Literature

Location	Soil	Month	OCS	CS <sub>2</sub>	Reference*
E and SE U.S.	histosol		2-46	0.2-260	1
Ohio	histosol	7	23	11	1
Ohio	histosol	7	6.9	1.4	2
Ohio	histosol	7	28	0.07	3
Iowa	mollisol	7	32	30	4
Iowa	mollisol	7	2.8	0.6	2
Iowa	mollisol	7	5.45	0.43	3
E and SE U.S.	mollisol/ alfisol/ inceptisol/ ultisol		0.38-55	1.9-42	1
Massachusetts	forrest	spring	6.0 19 14 18	1.4 1.2 1.6 15	5
Germany	organic	4-11	6-14	3-13	6
	other		2-10	1-12	
North Carolina	marsh	7/8/9	57	380	7
Cedar Isl. and N. C.	marsh	10	3.8		1
		5	19	17	
		7	38	114	
Cedar Isl. and N. C.	Marsh	8	8(4-15)	6(2-12)	2
Cedar Isl. and N. C.	marsh	8	30(12-72)	4(1-15)	3
Wallops Isl. and Va.	marsh		57	2600	1
Wallops Island Va.	marsh	8/9	2.7(0.3-7)		8
Massachusetts	marsh		7.6	53	1
Massachusetts	marsh		572	305	9
Cox's landing, N. C.	marsh	11	12100	1850	1
		7	1670		
E and SE U.S.	marsh		0.38-114	1.0-2090	1

Fluxes are in ngS m<sup>-2</sup> min<sup>-1</sup>.

\* References are 1, Adams et al. [1981]; 2, Goldan et al. [1987]; 3, Lamb et al. [1987]; 4, Adams et al. [1980]; 5, Melillo and Steudler [1989]; 6, Staubes et al. [1989]; 7, Aneja et al. [1979]; 8, Carroll et al. [1986]; 9, Steudler and Peterson [1984, 1985].

others, this can lead to large uncertainties in the measured flux. Furthermore, if the concentration inside the enclosure builds up to a level significantly higher than the concentration in the ambient air, the normal emission from the surface may be inhibited.

The reported flux values for OCS and CS<sub>2</sub> from soils and marshes are summarized in Table 2. The first comprehensive measurements in biogenic sulfur emissions, including OCS and CS<sub>2</sub>, were those reported by Adams et al. [1981]. They measured sulfur fluxes at 35 locations in the eastern and southeastern United States from 11 major soil orders. The range of fluxes for OCS and CS<sub>2</sub> reported by these authors were 0.0018-0.25 ng OCS m<sup>-2</sup> min<sup>-1</sup> and 0.0046-2.7 ng CS<sub>2</sub> m<sup>-2</sup> min<sup>-1</sup>, respectively. On the basis of these measurements, Khalil and Rasmussen [1984] estimated that 0.4 Tg(OCS) and 0.9 Tg(CS<sub>2</sub>) were emitted from soil each year. Three of the measurement sites (Iowa, Ohio, and North Carolina) examined by Adams et al. [1981] were subsequently revisited by Goldan et al. [1987], Lamb et al.

[1987] and MacTarggart et al. [1987] with the last group reporting only the total sulfur flux rather than the flux from individual sulfur compounds. Goldan et al. found that fluxes of OCS and CS<sub>2</sub> from soils were strongly correlated with air temperature, and their results were nearly an order of magnitude lower than the earlier measurements by Adams et al. [1981]. Independent studies conducted by Lamb et al. [1987] agreed with Goldan et al. within a factor of 2 to 3, while the total sulfur measurements by MacTarggart et al. [1987], at the same sites, also supported the lower values. Staubes et al. [1989] measured OCS and CS<sub>2</sub> fluxes from 12 representative soils in Germany, which also showed lower values than those reported by Adams et al. [1981]. Goldan et al. [1987] have suggested that the higher flux values from the earlier studies of Adams et al. [1981] may have been a consequence of insufficient waiting time after the emplacement of the flux chambers over the sampled surface area. Other possibilities include changes in microclimatological conditions from one set of measurements to the next.

Since all the above investigators were using sulfur-free air as the carrier gas in their dynamic enclosure systems, no uptake could be measured. More recently, Castro and Galloway [1991] presented measurements of OCS and CS<sub>2</sub> fluxes from forest soils at Shenandoah National Park, Virginia. They observed positive fluxes of both OCS and CS<sub>2</sub> [with the values comparable to the results of some of the previous studies of Goldan et al. [1987] and Lamb et al. [1987] when sulfur-free air was used. However, they observed negative fluxes for both sulfur compounds (ranging from 2.78 to 16.2 ngS m<sup>-2</sup> min<sup>-1</sup> for OCS and from 3.42 to 26.2 ngS m<sup>-2</sup> min<sup>-1</sup> for CS<sub>2</sub>) when ambient air was used as the carrier gas. Castro and Galloway concluded that large positive artifacts were inherent in the sulfur-free air technique. In fact, Castro [1990] has suggested that emissions from the soil may have been overestimated by 60% in the past. In contrast to Castro and Galloway's observations, Melillo and Steudler [1989] used the ambient air technique in measurements of OCS and CS<sub>2</sub> emissions from forest soils, with and without nitrogen fertilization, at Harvard Forest, Massachusetts. They observed all positive fluxes, ranging from 6.01 to 19.0 ng-S m<sup>-2</sup> min<sup>-1</sup> for OCS and from 1.17 to 15.3 ng-S m<sup>-2</sup> min<sup>-1</sup> for CS<sub>2</sub>. Thus these data once again suggest that considerable uncertainty remains about the magnitude of the COS and CS<sub>2</sub> source and sink from global soils.

The measurements of OCS and CS<sub>2</sub> fluxes from marshes, which are spatially and temporally much more variable, are also listed in Table 2. Steudler and Peterson [1984, 1985] used ambient air as the carrier gas to measure the fluxes of several sulfur species from a New England salt marsh over a period of one year. They found that annual fluxes of OCS and CS<sub>2</sub> were, respectively, 572 ngS m<sup>-2</sup> min<sup>-1</sup> and 305 ngS m<sup>-2</sup> min<sup>-1</sup> with no consistent diurnal emission patterns. Carroll et al. [1986], however, observed a clear diurnal variation of OCS emission from the salt water marsh at Wallops Island, Virginia; the diurnally averaged emission rate was found to be 2-3 orders of magnitudes lower than that found by Steudler and Peterson. The measurements at Cedar Island, North Carolina by Goldan et al. [1987] resulted in a flux that ranged from 4 to 15 ngS m<sup>-2</sup> min<sup>-1</sup> for OCS and from 2 to 12 ngS m<sup>-2</sup> min<sup>-1</sup> for CS<sub>2</sub>. These results are seen to be in agreement with the data obtained by Lamb et al. [1987] but are 1-2 orders of magnitudes lower than the value measured at the same site and season by Adams et al. [1981] and by Aneja et al. [1979a, b]. Morrison and Hines [1990] found that one type of marsh vegetation (*spartina patens*) emitted OCS while another type of marsh vegetation (*spartina alterniflora*) took up OCS.

In summary, the role of soils and marshes as a global source of OCS and CS<sub>2</sub> is not clearly defined at this time. Emission or uptake of the sulfur compounds by the soil or

marsh appears to be very much dependent on soil conditions such as temperature, soil moisture, and nitrogen content. Currently, though, there is still not enough experimental evidence to support the view that soils and marshes are a net sink of OCS and CS<sub>2</sub> on a global scale. The suggestion that OCS and CS<sub>2</sub> emissions may have been overestimated by 60% during the past [Castro, 1990] are based on measurements at only one site and for only one type of soil. Thus, it is difficult to extrapolate these results to the global scale. In this study, soils and marshes have been considered as net sources for OCS and CS<sub>2</sub>, although we acknowledge that it is quite possible that this picture may change in the future.

Our final estimate of the emissions of OCS and CS<sub>2</sub> from soils and marshes is based on the correlations of measured fluxes and the air temperatures reported by both Goldan et al. [1987] and Lamb et al. [1987]. These authors have conducted an extensive investigation on several different types of soil in which the correlations between the flux and the ambient temperature were obtained, and the results between these two groups agree reasonably well. Soils are characterized as organic (mainly histosol) and other (mollisol, alfisol, entisol, inceptisol, oxisol, utisol, vertisol and mountain soil). The relationship between sulfur emissions and the ambient temperature [Goldan et al., 1987; Lamb et al., 1987] is that given by (4)

$$\ln F = a + bT \quad (4)$$

where F is the sulfur flux, T is the ambient temperature in degree celsius, a and b are parameters that depend on the type of soil and sulfur compound. Total emissions from soils and marshes were thus calculated to be 0.27 (0.14-0.52) Tg(OCS) yr<sup>-1</sup> and 0.023 (0.012-0.045) Tg(CS<sub>2</sub>) yr<sup>-1</sup>, respectively.

### 2.3. Vegetation

The gas exchange between vegetation and the atmosphere usually involves transport across the outer surface (i.e., leaf surface) and inner surface (i.e., cell wall in contact with the intercellular space) of the vegetation. The exchange between the atmosphere and the inner surface is under the control of stomata whose opening is affected by many environmental factors such as humidity, light intensity and water stress [Wesely et al., 1989]. For many vegetation species, there is a compensation point, a level at which the ambient trace gas concentration is in equilibrium with metabolites within the plant cell. The gas is taken up by the vegetation when the ambient concentration exceeds the compensation point, and gas is emitted by vegetation when the concentration is less than the compensation point [see Wesely et al., 1989]. Similar to CO<sub>2</sub>, compensation points

exist for OCS and CS<sub>2</sub> that tend to be vegetation type dependent.

Dynamic enclosure measurements have shown that OCS can be emitted from vegetation and that these emissions could be the major sulfur compound emitted from deciduous and coniferous trees [Lamb et al., 1987; Guenther et al., 1989]. However, these measurements, which utilized sulfur-free air, do not necessarily reflect the potential for plants to uptake OCS. Results from laboratory studies have shown that OCS is taken up by growing vegetation [Taylor et al., 1983; Kluczewski et al., 1983, 1985; Fall et al., 1988; Goldan et al., 1988] and that this uptake may represent the major sink for atmospheric OCS [Brown and Bell, 1986; Goldan et al., 1988]. While some field observations support this hypothesis [Goldan et al., 1987; Mihalopoulos et al., 1989; Hofmann et al., 1992], there are other field measurements which show no evidence of uptake of OCS [Berresheim and Vulcan, 1992].

Unfortunately, there are even fewer studies involving CS<sub>2</sub> exchange between vegetation and air. In one study the deposition of CS<sub>2</sub> to laboratory grown vegetation has been reported to have taken place at a slower rate than for OCS [Taylor et al., 1983]. Goldan et al. [1987] has reported the net CS<sub>2</sub> emission from vegetated surfaces to be near zero. In this study, vegetation was considered to be a sink for OCS (see later section on "Sinks of OCS and CS<sub>2</sub>") and a null source of CS<sub>2</sub>.

#### 2.4. Volcanoes

The volcanic emissions of OCS were estimated to be 0.02 Tg(OCS) yr<sup>-1</sup> by Cadle [1980], 0.01-0.05 Tg(OCS) yr<sup>-1</sup> by Khalil and Rasmussen [1984] and, more recently, 0.006-0.09 Tg(OCS) yr<sup>-1</sup> by Belviso et al. [1986]. While very little CS<sub>2</sub> volcanic emission data has been reported, Khalil and Rasmussen [1984] estimated that the same amount of CS<sub>2</sub> was emitted from volcanoes as OCS. About 67% of the volcanoes in the world are in northern hemisphere, and approximately 18% are between 10°S and south pole [Simkins et al., 1981]. In this study the total volcanic source of 0.02 Tg for both OCS and CS<sub>2</sub> was adopted; the volcanic source distribution of OCS and CS<sub>2</sub> was assumed to be the same as the distribution of volcanoes in the world.

Thus, even though the magnitude of this source has considerable uncertainty, volcanoes appear to play only a minor role in the OCS and CS<sub>2</sub> budget on the global scale.

#### 2.5. Biomass Burning

About 90% of the biomass burned each year is due to human activities, for example, shifting agriculture, deforestation, firewood consumption, and burning agriculture wastes. While OCS is one of the trace gases produced from incomplete biomass burning (i.e., during the smoldering stage [Crutzen and Andreae, 1990]), no observation of CS<sub>2</sub> has ever been reported. The production of OCS from biomass burning is typically reported as the volume mixing ratio of OCS to CO<sub>2</sub>. For example, Crutzen et al. [1979] reported a OCS/CO<sub>2</sub> ratio of  $5.4\text{--}28.6 \times 10^{-6}$  from their measurements of the Wild Basin fire in Colorado; however, later measurements taken by Crutzen et al. [1985] in Brazil during the dry season showed a ratio of  $1.5\text{--}15 \times 10^{-6}$ . Other measurements in Africa by Bingemer et al. [1992] and Nguyen et al. [1990] showed that the OCS/CO<sub>2</sub> ratio from biomass burning was  $6\text{--}42 \times 10^{-6}$  and  $3\text{--}20 \times 10^{-6}$ , respectively. Table 3 summarizes all available OCS/CO<sub>2</sub> ratios, most of which were reported for tropical areas.

The total carbon released from biomass burning has been estimated recently by Andreae [1991] as 3910 TgC yr<sup>-1</sup> and by Crutzen and Andreae [1990] as 1800-4700 TgC yr<sup>-1</sup>. About 90% of the carbon released to the atmosphere is in the form of CO<sub>2</sub>. In this study, the total amount of OCS released from biomass burning was evaluated as a function of latitude and type of source, the average value for the ratio OCS/CO<sub>2</sub>, and the average amount of carbon released from different burning sources as estimated by Andreae [1991]. The latitudinal distribution of carbon released from each source was assumed to be the same as the areal distribution of the corresponding source. For example, the carbon released from burning of temperate forest in the four latitudinal regions (introduced in section 1) was assumed to be proportional to the area of temperate forest in those regions [Whittaker and Likens, 1975; Rand McNally World Atlas, 1984]. The distribution of the carbon released from agricultural waste was assumed to be proportional to that of

TABLE 3. Observed OCS/CO<sub>2</sub> Ratio From Biomass Burning

Location	OCS/CO <sub>2</sub>	Reference*
Wild basin fire, Colorado	$15.8(5.4\text{--}28.6) \times 10^{-6}$	1
Tropical forest, Brazil	$4.7(1.5\text{--}15) \times 10^{-6}$	2
Equatorial rain forest, northern Congo	$(6\text{--}42) \times 10^{-6}$	3
Savannah, Ivory Coast	$(3\text{--}20) \times 10^{-6}$	4

\*References are 1, Crutzen et al. [1979]; 2, Crutzen et al. [1985]; 3, Bingemer et al. [1990]; 4, Nguyen et al. [1990].

crop yields in those regions [U.S. Department of Agriculture, 1987]. And the distribution of carbon released from fuelwood combustion was taken to be proportional to fuelwood consumption in those regions [1990 Britannica Book of the Year]. The total OCS emission from biomass burning was estimated at 0.14 (0.04-0.26) Tg (OCS) yr<sup>-1</sup>.

The large range in the estimated amount of OCS released from biomass burning reflects the following uncertainties. First, while CO<sub>2</sub> is released during the firing stage, OCS is mainly released during the smoldering stage of biomass burning. Unfortunately, it is not clear how the amount of OCS and CO<sub>2</sub> released in these two different stages is correlated. Second, the measured OCS/CO<sub>2</sub> ratio may not represent the global situation because, as indicated in Table 3, most of the measurements were taken in tropical areas and measurements for some other important biomass burning, such as in boreal forest and from agriculture waste, were not available. Third, the amount of CO<sub>2</sub> released from biomass burning, used as the reference in estimating the OCS released from the same source, is itself still quite uncertain.

## 2.6. Anthropogenic Sources

**2.6.1. Chemical Industry Emissions (CS<sub>2</sub>).** The principal industrial use of CS<sub>2</sub> is in the manufacture of regenerated cellulose rayon and cellophane [Peyton et al., 1976; Timmerman, 1978; Lay et al., 1986] where CS<sub>2</sub> is employed as a solvent carrier to form xanthate crumb from alkali cellulose. During the spinning process, CS<sub>2</sub> is liberated and the viscose is coagulated and filaments of the regenerated cellulose are formed [Peyton et al., 1976; Shreve and Brink, 1977]. In this process, some portion of the CS<sub>2</sub> is converted into several nonvolatile by-products [Lundberg and Turbak, 1982]. Other uses of CS<sub>2</sub> include the synthesis of carbon tetrachloride (CCl<sub>4</sub>) and some industrial chemical production, as well as agricultural and pharmaceutical applications [Peyton et al., 1976; Timmerman, 1978; Lay et al., 1986].

While Peyton et al. [1976] estimated that greater than 80% of the CS<sub>2</sub> produced in the United States was used to make regenerated cellulose rayon and cellophane, Timmerman [1978] indicated that of the total CS<sub>2</sub> production in the United States in 1974 only 33% was used in rayon manufacturing, 13% in the cellophane film production, and 31% in the CCl<sub>4</sub> production. The remaining 23% was distributed over many other uses in which CS<sub>2</sub> was used either as a reactant or as a solvent. More recent information has been provided by Lay et al. [1986] for the world production and use of CS<sub>2</sub>. He has estimated that in 1984 the worldwide production of CS<sub>2</sub> was 1.085 Tg. Of

this total, over 65% was used in manufacturing rayon, about 10% in making cellophane, and 10% in CCl<sub>4</sub> production, and the remaining 15% was distributed among rubber chemicals, pesticides, and chemical reagents. In general, the worldwide production of CS<sub>2</sub> appears to parallel the production of rayon [Timmerman, 1978], and since the latter has been near constant for the time period of 1965 to 1980 [Lundberg and Turbak, 1982], this is reflected in the total world production of CS<sub>2</sub> being reasonably stable.

The only estimate of CS<sub>2</sub> released to the atmosphere from chemical production of CS<sub>2</sub> was that reported 16 years ago by Peyton et al. [1976]. These authors estimated that about 38% of the CS<sub>2</sub> used in the United States in 1974 was emitted to the atmosphere. In this study, the following assumptions were made in estimating the global emission from the chemical production of CS<sub>2</sub>: (1) The worldwide production and the percentage use of CS<sub>2</sub> for different applications as given by Lay et al. [1986] is representative of the current global configuration. (2) That of the CS<sub>2</sub> used in the cellulosic industry (75% of the total CS<sub>2</sub> production) 20% is emitted to the atmosphere in the United States and western Europe (due to more restrictive environmental regulations) while 40% is emitted to the atmosphere in the remainder of the world. (3) Half of the CS<sub>2</sub> used in applications other than in cellulosic and CCl<sub>4</sub> production (e.g., 7.5%) is assigned to some form of solvent applications; and, of this, we estimate 80% is released into the atmosphere because of its high volatility and relatively low solubility in water. Thus the CS<sub>2</sub> released from the chemical production of CS<sub>2</sub> was estimated using the expression

$$F_{\text{CS}_2} = (P_{\text{CS}_2} \times 0.75 \times f) + (P_{\text{CS}_2} \times 0.075 \times 0.80) \quad (5)$$

where  $F_{\text{CS}_2}$  designates the amount of CS<sub>2</sub> released from industrial sources,  $P_{\text{CS}_2}$  is the chemical production of CS<sub>2</sub>, and  $f$  is the release factor for CS<sub>2</sub> from the cellulosic industry which is 0.20 for United States and western Europe, and 0.40 for the rest of the world. The first term on the right-hand side of (5) shows that 75% of the CS<sub>2</sub> is used in the cellulosic industry, while the second term reflects the amount of CS<sub>2</sub> released from other solvent applications. In this study, the total amount of CS<sub>2</sub> released from the chemical production of CS<sub>2</sub> was found to be 0.31 (0.16-0.47) Tg(CS<sub>2</sub>) yr<sup>-1</sup>.

**2.6.2. Coal combustion.** While it is not believed to be a source of CS<sub>2</sub>, coal combustion from power plants has been identified as a source of OCS [Khalil and Rasmussen, 1984]. The emission ratio of OCS/CO<sub>2</sub> from a power plant in Denver, Colorado was found to be  $(2.3 \pm 0.7) \times 10^{-6}$  by Khalil and Rasmussen [1984]. If this OCS/CO<sub>2</sub> ratio is



applied worldwide to coal combustion, the amount of OCS from this source can be estimated from the CO<sub>2</sub> released from the same source. In this study, the total coal burned annually was taken to be  $4.54 \times 10^{15}$  g [1989 data, from *1990 Britannica Book of the Year*], of which 69% (by weight) has been estimated as released as CO<sub>2</sub> [Rotty, 1983]. The global OCS emission from coal combustion was thus evaluated to be 0.036 Tg(OCS) yr<sup>-1</sup>. The uncertainties here are similar to those found in biomass burning, i.e., in the representativeness of the measured OCS/CO<sub>2</sub> ratio, and in the amount of CO<sub>2</sub> released worldwide.

**2.6.3. Sulfur recovery.** Both OCS and CS<sub>2</sub> can be produced in sulfur recovery processes which primarily involve oil refinery and natural gas processing facilities [Peyton et al., 1976]. Because of various state and local regulations, sulfur recovery units are often installed to convert the remaining sulfur compounds (mainly H<sub>2</sub>S) from oil refineries and natural gas processes to elementary sulfur instead of burning them which would result in SO<sub>2</sub> emission. This sulfur recovery process produces OCS and CS<sub>2</sub> because of the presence of hydrocarbons. A small amount of the generated OCS and CS<sub>2</sub> can escape to the atmosphere even after tail gas treatment [Peyton et al., 1976]. The emission of OCS and CS<sub>2</sub> from the sulfur recovery process estimated in this study is based on the study by Peyton et al. [1976], assuming that these emissions are proportional to the oil refinery and natural gas processing capacities and assuming that all other countries had the same percentage (20%) of tail gas treatment as did the United States at the time of the investigation by Peyton et al. in 1974. The information on the relevant industrial capacities was found in the *United Nations Statistical Yearbook*. The total amount of OCS and CS<sub>2</sub> emitted from the sulfur recovery processes was estimated in our study to be 0.0019 (0.001-0.0038) Tg(OCS) yr<sup>-1</sup> and 0.0026 (0.0013-0.0052) Tg(CS<sub>2</sub>) yr<sup>-1</sup>.

**2.6.4. Automobile emissions.** Automobiles have been shown to emit OCS and CS<sub>2</sub>. Peyton et al. [1976] estimated the conversion factors for OCS and CS<sub>2</sub> from the sulfur

content in automotive gasoline to be 0.06 and 0.003, respectively. Recently, Fried et al. [1992] measured OCS emissions from a variety of automobiles and found a very high correlation between OCS and CO emission rates. On the basis of their measurements, Fried et al. estimated global OCS emissions from automobiles to range between 0.0008 to 0.008 Tg(OCS) yr<sup>-1</sup>. A mean value of 0.004 Tg(OCS) yr<sup>-1</sup> was adopted in this study. The CS<sub>2</sub> emission was estimated to be 0.00033 Tg(CS<sub>2</sub>) yr<sup>-1</sup>, based on the conversion factors of the gasoline sulfur content to OCS and CS<sub>2</sub> and on the emission rate relative to that of OCS [Peyton et al., 1976]. The uncertainties were estimated to be a factor of 2 for both OCS and CS<sub>2</sub>.

**2.6.5. Other.** Although there are several other anthropogenic sources for OCS and CS<sub>2</sub>, for example, paper industry [Himberg et al., 1987], fish processing, starch manufacturing, [Graedle et al., 1986], these sources cannot be quantified at this time. And as was suggested by Turco et al. [1980], they are probably not important and have thus been assigned a value equal to or less than 0.005 Tg(OCS) yr<sup>-1</sup>.

## 2.7. OCS From CS<sub>2</sub> conversion

The atmospheric reaction of CS<sub>2</sub> with OH is a source of OCS as well as the dominant sink for CS<sub>2</sub> in the atmosphere. The molar conversion factor for OCS from CS<sub>2</sub> has been convincingly established as  $0.81 \pm 0.06$  [Chin, 1992] while the global source strength of CS<sub>2</sub> (arithmetical) has been estimated in this study to be 0.54 (0.27-0.97) Tg(CS<sub>2</sub>) yr<sup>-1</sup>. The latter CS<sub>2</sub> source strength indicates that there is an additional 0.34 (0.17-0.61) Tg(OCS) yr<sup>-1</sup> source from the atmospheric oxidation of CS<sub>2</sub>.

## 2.8. Estimation of Total Source Range for OCS and CS<sub>2</sub>

The fact that there are large uncertainties in each of the natural and anthropogenic sources estimated for CS<sub>2</sub> and OCS creates a potentially wide range of answers in any evaluation of the global source strength for these two sulfur

TABLE 4a. Estimated Global Sources of OCS and CS<sub>2</sub>

sources	Tg(OCS), yr <sup>-1</sup>	Tg(CS <sub>2</sub> ), yr <sup>-1</sup>
Ocean	0.32(0.16-0.64)	0.18(0.09-0.36)
Soil and marsh	0.27(0.14-0.52)	0.023(0.012-0.045)
Volcano	0.02(0.006-0.09)	0.02(0.006-0.09)
Biomass burning	0.14(0.04-0.26)	
Coal combustion	0.036(0.025-0.047)	
Chemical production		0.31(0.16-0.47)
Sulfur recovery	0.002(0.001-0.004)	0.0026(0.0013-0.0052)
Automobile	0.004(0.001-0.008)	0.0003(0.0002-0.0006)
CS <sub>2</sub> conversion	0.34(0.17-0.61)	
Total (arithmetical)	1.14(0.55-2.19)	0.54(0.27-0.97)
Total (statistical)	1.23(0.83-1.71)	0.57(0.34-0.82)

TABLE 4b. Estimated Global Sinks of OCS and CS<sub>2</sub>

sinks	Tg(OCS) yr <sup>-1</sup>	Tg(CS <sub>2</sub> ) yr <sup>-1</sup>
Reaction with OH	0.13(0.02-0.80)	0.57(0.34-0.82)
Reaction with O	0.015(0.009-0.026)	negligible
Photolysis	0.029(0.020-0.040)	negligible
Vegetation uptake	0.43(0.16-1.0)	
Total (arithmetical)	0.58(0.19-1.77)	0.57(0.34-0.82)
Total (statistical)	0.79(0.30-1.52)	0.57(0.34-0.82)

species. The upper and lower limits ( $S_{\max}$  and  $S_{\min}$ ) quoted in the literature for the total source strength typically represent the simple sum of the minima and maxima of the individual sources, for example,

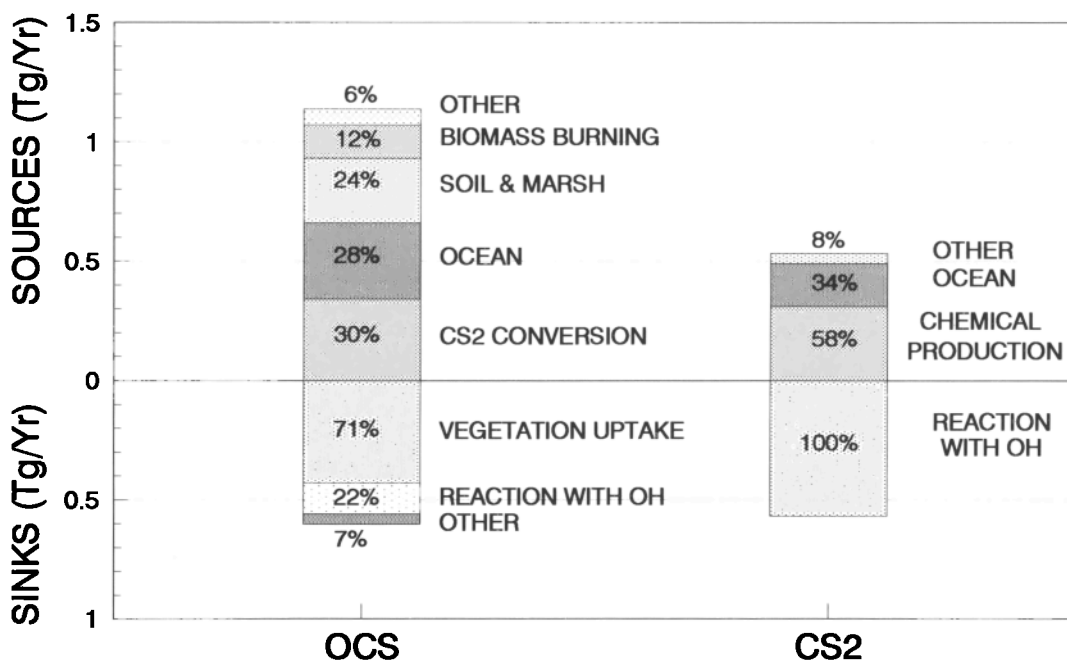
$$S_{\min} = \sum_k S_{k,\min}, \quad S_{\max} = \sum_k S_{k,\max} \quad (6)$$

where  $k$  defines the individual sources. The best estimate of the total source is then given by the arithmetical sum of the best estimates of the individual sources.

Summarized in Table 4 and illustrated graphically in Figure 1 are the results from this work for the sources and sinks of OCS and CS<sub>2</sub> based on the simple arithmetical approach. In the case of OCS the arithmetical median for the total global source was estimated to be 1.14 Tg(OCS) yr<sup>-1</sup> and the range was 0.55 to 2.19 Tg(OCS) yr<sup>-1</sup>. For CS<sub>2</sub> the arithmetical median was 0.54 Tg(CS<sub>2</sub>) yr<sup>-1</sup>, and its range was 0.27 to 0.97 Tg(OCS) yr<sup>-1</sup>. The latitudinal source distributions for OCS and CS<sub>2</sub> are shown in Figures 2 and 3.

In this study we also have applied a statistical method in estimating the median and the range of the total source and sink strength for OCS and CS<sub>2</sub>. As pointed out by Khalil [1990], the total range estimated using an arithmetical approach is unrealistically large. He has argued, and we believe correctly so, that the total source strength and range should be based on a statistical analysis of the individual sources and their respective uncertainties. A full description of this method has been given by Khalil [1990]; thus we have limited our comments here to the application of the method to this study.

It can be seen in Table 4 that the best estimate value for each individual source is typically not found to be centered in the range of values for that source. In each case therefore we have assumed that the best estimate value was the median value such that the total probability for each individual source less than the median was 1/2 and that greater than the median value was also 1/2. For convenience of computation, the sources were given in discrete steps,  $\Delta s$ , of size 0.01 Tg yr<sup>-1</sup>. The probability

Fig. 1. Estimated global sources and sinks for OCS and CS<sub>2</sub>.

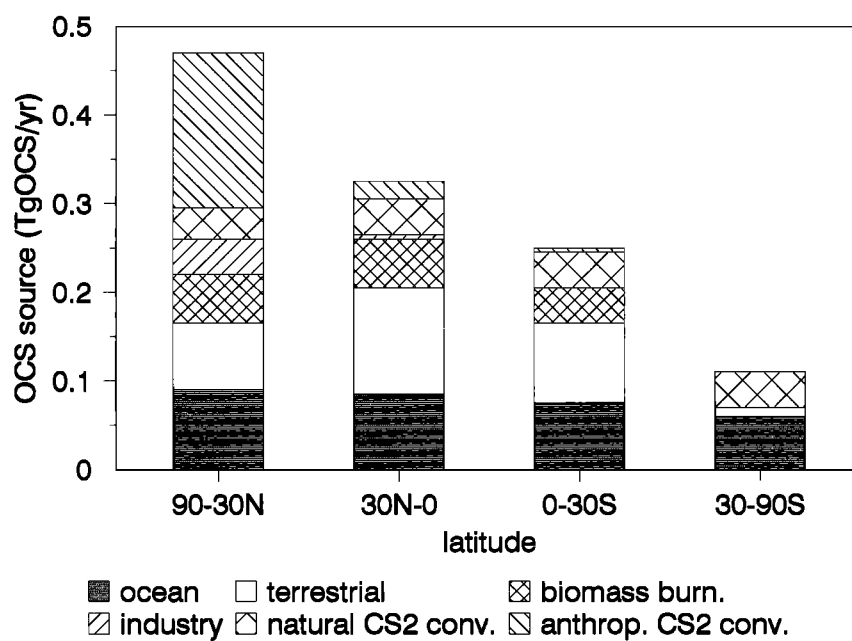
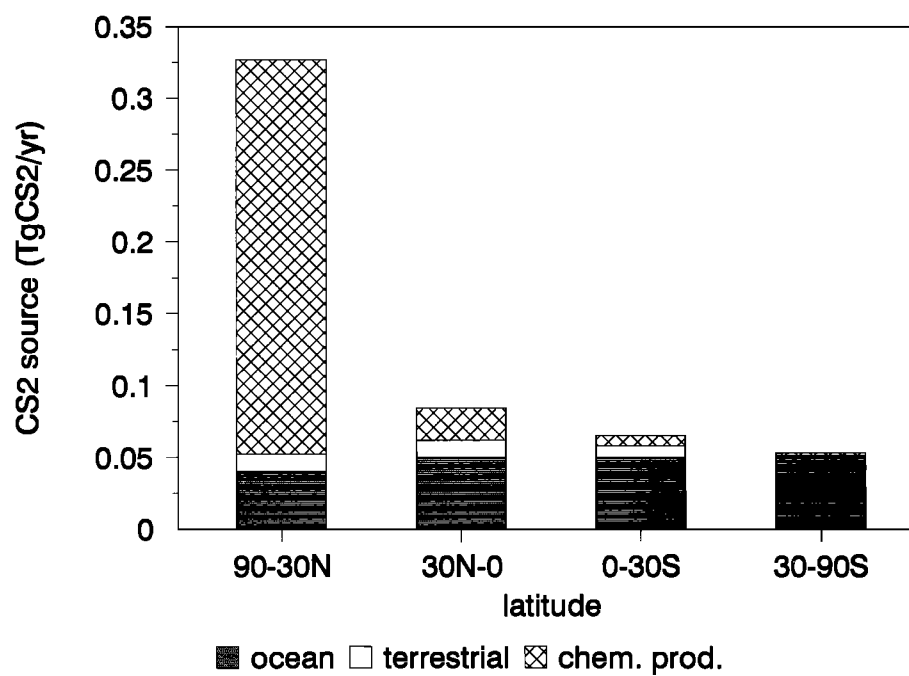


Fig. 2. Estimated COS source distribution

Fig. 3. Estimated CS<sub>2</sub> source distribution

distribution function (PDF) for source  $k$  was thus defined so that the probability of finding a value between  $S_k$  and  $S_k + \Delta S$  was  $P_k(S_k)\Delta S$ ; for example,

$$\sum_{S_{k,\min}}^{S_{k,\text{median}}} P_k(S_k)\Delta S = \frac{1}{2}, \quad \sum_{S_{k,\text{median}}}^{S_{k,\max}} P_k(S_k)\Delta S = \frac{1}{2} \quad (7)$$

It was also assumed that the PDF for source  $k$  was uniformly distributed between  $S_{k,\min}$  and  $S_{k,\text{median}}$  and also between  $S_{k,\text{median}}$  and  $S_{k,\max}$ . The best estimate value for the total source was defined by the median of the cumulative probability distribution constructed from the PDFs of the individual sources. For OCS this best estimate statistical source strength was evaluated to be 1.23 Tg(OCS) yr<sup>-1</sup>. The range for the total source at the 95% confidence level was 0.83-1.71 Tg(OCS) yr<sup>-1</sup>. For CS<sub>2</sub> the source strength was evaluated to be 0.57 Tg(CS<sub>2</sub>) yr<sup>-1</sup> with a range of 0.34 - 0.82 Tg(CS<sub>2</sub>) yr<sup>-1</sup> (95% confidence level). From table 4, it can be seen that for both species the statistical approach gives a somewhat higher best estimate value and a significantly reduced range than that derived from the simple arithmetical summation method.

Previously, Khalil and Rasmussen [1984] estimated that the total source strength of OCS and CS<sub>2</sub> were both approximately 2 Tg yr<sup>-1</sup>. The difference between their results and those reported here is mainly due to significant differences in several of the individual sources. In Khalil and Rasmussen's work, there was a much higher estimated flux from the ocean and soil, for example, 0.6 Tg yr<sup>-1</sup> for the oceanic flux for both OCS and CS<sub>2</sub>, and 0.4 and 0.9 Tg yr<sup>-1</sup> for the soil source. In their evaluation, Khalil and Rasmussen used Rasmussen et al.'s [1982] OCS ocean data and the early soil flux estimates reported by Adams et al. [1981]. The direct anthropogenic source of OCS estimated by Khalil and Rasmussen (0.14 Tg(OCS) yr<sup>-1</sup>) was also much higher than that estimated in this study, for example, 0.047 Tg(OCS) yr<sup>-1</sup>.

### 3. SINKS OF OCS AND CS<sub>2</sub>

#### 3.1. Carbon Disulfide

The major sink for CS<sub>2</sub> is its reaction with tropospheric OH radicals. On the basis of its reaction with OH, the lifetime of CS<sub>2</sub> is a few days, depending on the average level of OH. Although CS<sub>2</sub> can also be photolyzed by solar UV radiation, this photolysis rate becomes significant only at altitudes above 5-6 km [Chin, 1992] where there tends to be very little CS<sub>2</sub> present due to its low altitude destruction by OH. The reaction of CS<sub>2</sub> with O atoms is negligible because of the very low O atom concentration in the troposphere.

#### 3.2. Carbonyl Sulfide

**3.2.1. Photochemical reactions.** Carbonyl sulfide can be photochemically decomposed in the atmosphere by solar UV radiation having a wavelength  $\leq 388$  nm. The calculated global diurnally and seasonally averaged OCS loss by photodissociation was found to be 0.027 Tg(OCS) yr<sup>-1</sup> in the stratosphere and 0.0016 Tg(OCS) yr<sup>-1</sup> in the troposphere. These destruction rates are based on OCS photodissociation rates calculated from a multistream radiative transfer model (i.e., discrete ordinate) and the stratospheric and tropospheric concentrations of OCS. The stratospheric altitudinal OCS profile used for the calculation of OCS loss was based on observations of Inn et al. [1979, 1981], Louisnard et al. [1983], Zander et al. [1988], and Leifer [1989] and one-dimensional model calculations. Details concerning this photodissociation process and the corresponding calculations are discussed by Chin [1992].

Other photochemical removal processes for OCS involve the reactions of OCS with O and OH in both the stratosphere and the troposphere. These chemical loss rates have been evaluated of OCS has been calculated by Chin [1992]. The results from the latter calculations have indicated that the total loss of OCS due to reaction with OH and O in the troposphere and the stratosphere is 0.13 and 0.015 Tg(OCS) yr<sup>-1</sup>, respectively.

**3.2.2. Vegetation uptake.** As discussed earlier in the text, laboratory studies have shown that OCS is readily taken up by growing vegetation. Goldan et al. [1988] conducted laboratory studies of OCS uptake by agriculture crops under controlled conditions of light intensity, temperature, and CO<sub>2</sub> concentration. Their measurements indicated that the major uptake pathway was through open stomata. Similarities in the uptake resistance between OCS and CO<sub>2</sub> led these authors to suggest that the global OCS uptake could be estimated from the global terrestrial primary productivity resulting from CO<sub>2</sub> uptake. Furthermore, in a recent investigation of the enzymatic pathways for the uptake of OCS by higher plants, Protosc-hill-Krebs and Kesselmeier [1992] demonstrated that all enzymes involved in CO<sub>2</sub> assimilation by higher plants can also metabolize OCS. For example, the measurements over a wheat field in Germany by Hofmann et al. [1992] showed a positive correlation between OCS uptake and CO<sub>2</sub> uptake. Kesselmeier [1992] suggested that the strength of OCS uptake by vegetation could be evaluated using a vegetation type dependent deposition ratio of OCS/CO<sub>2</sub> in combination with net primary production from different ecosystems. The latter author has estimated that the vegetation uptake strength could be as high as 1 Tg (OCS) yr<sup>-1</sup> (J. Kesselmeier, personal communication, 1993).

In this study, the deposition velocity of OCS and that of CO<sub>2</sub> were taken as approximately the same; the ratio of the

uptake of OCS and CO<sub>2</sub> was therefore the same as the ratio of their respective atmospheric concentrations. Although this represents a very large extrapolation to the global scale, it would appear to provide a useful estimate of the magnitude and distribution of the surface sink for OCS. Like CO<sub>2</sub>, the uptake of OCS is terrestrial ecosystem type dependent; thus for each ecosystem type "i," we have assumed that:

$$(\text{uptake of OCS})_i = (\text{uptake of CO}_2)_i \times [\text{OCS}] / [\text{CO}_2]$$

where [OCS] and [CO<sub>2</sub>] are the atmospheric concentrations of OCS and CO<sub>2</sub>, respectively. By adopting as the net primary production for terrestrial ecosystems the value defined by Whittaker and Likens [1975] and Ajtay et al. [1979] (including rain forest, seasonal forest, boreal forest, woodland, savanna, grass land, tundra, swamp and marsh, and cultivated land), the annual OCS uptake by vegetation was estimated to be 0.43 Tg(OCS) yr<sup>-1</sup>, with a range of 0.16-0.91 Tg(OCS) yr<sup>-1</sup>. The authors note that the distribution of OCS uptake for each ecosystem type "i" for the four latitudinal regions of this study were scaled to the areal distributions of the corresponding ecosystems. Our global estimate for the uptake of OCS from vegetation is comparable to the value estimated by Goldan et al. [1988] i.e., 0.24-0.59 Tg(OCS) yr<sup>-1</sup>. Like Goldan et al. [1988], we also have concluded that vegetation uptake is the major sink for atmospheric OCS (71%). The same statistical method used for analyzing the total source strength was also applied to the evaluation of the total sink. The median value obtained was 0.79 Tg(OCS) yr<sup>-1</sup> with the range of 0.30-1.52 Tg(OCS) yr<sup>-1</sup> (95% confidence level). In this case even though the best estimated sink strength does not balance the total estimated source strength (e.g., 1.23 Tg(OCS) yr<sup>-1</sup> with a range of 0.83-1.71 Tg(OCS) yr<sup>-1</sup>), the source and sink for OCS are seen to agree within their stated uncertainty ranges.

#### 4. SUMMARY AND CONCLUSIONS

The final results of our inventory of global sources of OCS and CS<sub>2</sub> are listed in Table 4 and shown graphically in Figure 3. On the basis of the arithmetical sum of the individual sources, these results indicate that natural sources of OCS define 52% of the total source strength with 28% being defined by the ocean and 24% being derived from terrestrial sources (soil, marshes, and volcanoes). Biomass burning is the one major direct anthropogenic source of OCS (12%), with all other direct anthropogenic sources of OCS constituting less than or equal to 4%. The oxidation of CS<sub>2</sub> contributes 30% to the total OCS source. The total

anthropogenic component of the OCS source, mainly from conversion of anthropogenic CS<sub>2</sub>, is approximately 32%. Concerning CS<sub>2</sub>, it can be seen that the chemical industrial emissions of CS<sub>2</sub> are overall the major source (58%) while other anthropogenic CS<sub>2</sub> sources are nearly negligible (0.5%). The ocean is the major natural source of CS<sub>2</sub>, 34% of the total, whereas natural terrestrial sources contribute only 4% to the total CS<sub>2</sub> source strength.

On the basis of a statistical analysis of the best estimate values and ranges of all OCS and CS<sub>2</sub> sources and sinks, we estimate that the global source strength for OCS is 1.23 (0.83-1.71) Tg(OCS) yr<sup>-1</sup>, and that for CS<sub>2</sub> is 0.57 (0.34-0.82) Tg(CS<sub>2</sub>) yr<sup>-1</sup>. The corresponding sink values are 0.79 (0.30-1.52) Tg for OCS and 0.57 (0.34-0.82) Tg for CS<sub>2</sub>.

From available tropospheric measurements of OCS over the past 12-15 years [e. g., Sandalls and Penkett, 1977; Torres et al., 1980; Johnson and Harrison, 1986; Johnson et al., 1990; Bingemer et al., 1990; Bandy and Thornton, 1992], no secular trend in OCS tropospheric levels can be found. On the basis of several years of stratospheric aerosol measurements, Hofmann [1990] has concluded that for the time period 1979 to 1989 a  $5 \pm 2\%$  per year increase in stratospheric aerosol has occurred. The suggestion was therefore made that increases in anthropogenic OCS may have been responsible for this increase. Given a nominal 2% per year increase in stratospheric sulfur, this would convert to a 6%/yr increase in anthropogenic OCS since according to our inventory anthropogenic OCS is 34% of the global yearly source strength of OCS. Given the above scenario, for the time period 1979 to 1991 (during which time OCS measurements have been routinely reported) the total increase in the OCS ambient concentration level should have been ~24%. The fact that available atmospheric observations do not show a systematic increase in OCS levels strongly indicates that the anthropogenic source has not significantly increased during this time period. This observation, in fact, is consistent with the results from this inventory which shows that the major anthropogenic source of OCS is that resulting from the conversion of anthropogenic CS<sub>2</sub> (chemical industrial emissions) which appears to have been relatively stable over the past 25 years. In other words, the earliest reported OCS measurements (e.g. 1977) occurred nearly 10 years after the onset of the major anthropogenic release of CS<sub>2</sub>.

The latitudinal source distributions for both OCS and CS<sub>2</sub> show a significant northern to southern hemispheric gradient. The northern to southern hemispheric ratio for the source strength of OCS ranges from 1.9 to 2.4, with the "best estimate" value being 2.26. This gradient primarily reflects the much larger anthropogenic source and to a somewhat lesser extent the larger terrestrial soil/marsh OCS source in the northern hemisphere. In the case of CS<sub>2</sub>, we

find a north to south gradient that ranges from 3.0 to 3.6 with the "best estimate" being 3.4. As was true for OCS, this strong CS<sub>2</sub> gradient favoring the northern hemisphere is primary due to the much larger anthropogenic source in this hemisphere.

As indicated in the main body of the text, many uncertainties still exist in our assessment of the global sources and sinks of OCS and CS<sub>2</sub>. To remove these uncertainties, several types of studies are recommended.

1. More reliable methods are needed for evaluating surface fluxes of OCS and CS<sub>2</sub>. While the micrometeorological and eddy-correlation methods for measuring the vertical fluxes seem promising and are becoming available [H. Berresheim, private communication, 1991], innovative testing procedures, using conventional enclosure methods, are also needed to determine the credibility of earlier measurements. With respect to reducing the uncertainty in the evaluation of the ocean OCS flux, an expanded OCS data base is needed involving more seasonal data in both high- and low-productivity waters and an improved evaluation of the transfer velocity would also be extremely valuable.

2. There is a need for more comprehensive identification and quantification of all anthropogenic sources of OCS and CS<sub>2</sub>. For example, there are very few measurements of OCS emissions from biomass burning, and information on CS<sub>2</sub> from this source is nonexistent. High concentrations of both CS<sub>2</sub> and OCS have been observed in polluted air but the specific sources have never been identified. Most importantly, although the amount of CS<sub>2</sub> released from chemical industrial emissions (especially its use in the cellulosic industry) has been estimated to be the most important source of CS<sub>2</sub> (contributing >50% to the total CS<sub>2</sub> source and >17% to the total OCS source), detailed information on the release of CS<sub>2</sub> to the atmosphere from this source is very fragmentary with virtually no CS<sub>2</sub> measurements being reported in the vicinity of such a chemical facility.

3. More studies of OCS surface sinks are needed. Surface vegetation appears to be a major sink for OCS, but there is still conflicting information concerning the roles of vegetation and soil. Even though there are similarities in the biological response of vegetation between OCS and CO<sub>2</sub> in the laboratory, simultaneous measurements of both OCS and CO<sub>2</sub> are needed in the field. In addition, CS<sub>2</sub> uptake by vegetation and soil needs to be more extensively investigated.

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- Mian Chin and D. D. Davis, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332.

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